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Performance of Eleven Ti Alloys in High Temperature, High Pressure Brine Solution

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ABSTRACT

There is currently increasing interest in titanium alloys for geothermal production well casings due to their combination of strength, low density and corrosion resistance. These alloys may be able to augment the current list of commonly used materials available to resist corrosion and stress corrosion cracking in high temperature, high pressure sour brines. A total of eleven titanium alloys have been studied with four having platinum group metal additions.

There is data on nickel based alloys and low strength titanium alloys like Ti Gr7 at high temperature in sour brines, however there is little data on the behavior of new high strength titanium alloys in these environments to qualify their use. This paper will present the performance of eleven titanium alloys with respect to corrosion rate, and crevice corrosion susceptibility in high temperature, high pressure brine environments. The paper will also address the ability to weld and form titanium alloys intended for brine solutions.

1. INTRODUCTION

Titanium has been used for over 40 years in many corrosive applications such as chemical processing, refineries, metal finishing and pulp and paper. More recently titanium alloys have been used in the power generation industry, such as geothermal wells and oil and gas applications requiring higher strengths and good corrosion resistance. The conditions encountered in these geothermal, oil and gas applications include high temperatures and pressures combined with high concentration of dissolved solids which make the environment especially corrosive. It is also expected that in some applications there will be significant levels of acid gases such as H_2S and CO_2 which affects the more common downhole materials.

This paper will review the higher strength titanium alloy grades considered for use in heavy brine applications and compare them to titanium grades 2 and 7 and nickel-based alloys like Alloy 625, 276, etc. The performance of the eleven titanium alloys will be analyzed with respect to corrosion rate, and crevice corrosion susceptibility in high temperature, high pressure brine environments. The paper will also address the ability to weld and form titanium alloys intended for brine solutions.

2. TITANIUM CHARACTERISTICS

ASTM has registered 38 grades of titanium, however only a handful are commonly used in industry. Their strength to weight ratio makes titanium alloys ideal for aerospace applications as well as offshore heat exchangers. The thermal conductivity is 30% greater than 300 series stainless steel. The grades range from the commercially pure (Gr 1-4) to alloys with multiple added elements like Gr32 (Ti-5Al-1Sn-1Zr-1V-0.8Mo-0.1Si).

2.1 Mechanical Properties

The strength of titanium will depend on its alloying elements. Table 1 below summarizes several titanium alloys and other metals for comparison.

Table 1. Comparison of Corrosion Resistant Alloys

ASTM Grade	Ultimate ksi	Yield (0.2%)ksi	Elong. %
Ti Gr2	50	40	20
Ti Gr5	130	120	10
Ti Gr7	50	40	20
Ti Gr9	90	70	15
Ti Gr12	70	50	18
316 SS	85	30	40
Alloy 625	115	60	30

With increased strength comes reduced formability; however manufactures continue to search for an alloy with high strength, formability and weldability. One such alloy is Gr38, slightly less strength (115 ksi) than Gr5, but it can be readily formed cold and welded, Kerr et al. (2005).

Formability of materials can often be a remedy for a project with tight budget constraints compared to extruding large diameter pipe. Cal Energy discovered significant cost savings in ordering duplex stainless steel for their return lines in the rolled and welded form versus the seamless option. Similarly they purchased welded Gr12 titanium tubes instead of seamless for a condenser, Eberle and Furmanski (2009). Perhaps a cost saving can be found with a high strength titanium alloy with better corrosion resistance that is also formable. This study will check for cracking of welded coupons using a 10T bend test.

All the materials shown in Table 1 are readily available in cast, forged blocks, bars, sheet, plate, and tubes. One exception is with Gr5, the material is so inherently strong that it cracks when attempting to fabricate into tubes. Any heavy forming work requires working the material at elevated temperatures.

2.2 Corrosion Properties

Titanium exhibits excellent corrosion resistance in oxidizing chloride environments, which led to some of its first applications in the chemical process industry over 30 years ago. Other alloy compositions are still being developed and this study will evaluate two of these newer alloys.

The corrosion resistance of titanium relies on the formation of a thin oxide film, which occurs spontaneously in air or water. Once the oxide film is compromised, damage may occur. Reducing acids are often the cause of general corrosion on titanium. The corrosion resistance of titanium in reducing acids (hydrochloric, sulfuric, phosphoric, sulfamic, etc.) will depend on concentration and temperature. When Ti Gr2 will not work because of concentration or temperature concerns other titanium alloy grades like Gr12 may be viable alternatives, Schutz and Grauman (1986). There are other limitations that can cause problems with titanium such as crevice corrosion. Although Ti Gr5 and Gr2 can suffer crevice corrosion in high temperature hypersaline brines, no crevice attack occurred on Gr2 when low to medium (< 15,500 ppm) chloride brines were tested, Thomas (2003). Other corrosion resistant metals like stainless steel and nickel-base alloys can suffer localized attack when chloride levels exceed 5,000 ppm and with temperatures greater than 100ºC. Consideration for titanium over stainless steel and nickel-base alloys is promoted when oxygen intrusion is possible, Thomas (2003).

Another alternative to increase titanium's corrosion resistance is to add small amounts of a Platinum Group Metal (PGM), typically palladium or ruthenium. The PGM addition has no effect on mechanical properties, but enhances corrosion resistance of the material in chlorides and extends the range of performance in mildly reducing environments. A common use of these grades is for gasket faces and crevices where Gr2 might be subject to crevice corrosion or pitting under NaCl deposits, Blauvelt et al. (2000).

3. APPLICATION AREAS

The adverse conditions in a geothermal well are obvious. The search for better materials will progress as deeper and more corrosive conditions emerge. Typical convective hydrothermal energy reaches temperatures in the 260-330°C range. New advances in the industry could lead to magma based energy where temperatures exceed 500°C. Alaska and Hawaii are likely locations for this to start, Sanyal (2009).

Other areas that may not seem so obvious but appear to favor titanium for its corrosion resistance include oil and gas production for offshore systems, refineries, gas fired power plants, and nuclear waste repositories.

3.1 Offshore

Titanium is a likely candidate for additional applications on offshore systems as the industry pushes to go into deeper waters. Ti alloys are attractive because their density is 60 percent of that of steel. The weight savings with higher strength materials means increased load carrying capacity, decreased wall thickness and section size. With proper heat treatment, sufficient yield strengths have been obtained for risers and swivel components. Additional savings come in the fact that titanium does not require corrosion inhibitors for production environments containing H_2S and high levels of CO_2. Long term reliability is also key with offshore systems that must last 30 plus years and a single deep water failure can result in direct and associated costs in the range of $10 to 100 million, Kane et al. (2000).

3.2 Petroleum

Due to their corrosion resistance, titanium alloys have been successfully used in various petroleum refining and petrochemical manufacturing process. Most applications chose Gr2 titanium. However, there are more applications evolving that require stronger alloys with better corrosion resistance to handle the process side corrosion. One example is Gr12 for atmospheric crude distilling column overhead condensers operating at 171°C. Other example applications of titanium grades 2, 7, 12 and 16 are in fractionator overhead condenser and sour water strippers, Fan et al. (2000).

3.3 Mining

The mining industry has been using titanium for over 50 years. It has found applications in leaching and electrowinning processes for metals including nickel, uranium, cobalt, copper and noble metals. To deal with problems, improvements have been realized using adoptive design and fabrication, or by switching to PMG containing alloys. In some cases, oxygen-rich environments or dramatic process condition changes can ignite titanium. To reduce this occurrence Gr36 titanium is a preferred choice. A direct example of this need is in recovering gold in a sulfide pressure oxidation process, Yau (1997). Ti Gr36 has also been tested for its performance in high temperature brine solutions.

3.4 Nuclear

In some nuclear applications the simple addition of PMG to Gr2 provides sufficient corrosion resistance. One such case is in Ti Gr7 drip shields used in the repository at Yucca Mountain. The expected lifetime is over 10,000 years because stress corrosion cracking, localized corrosion and microbiological influenced corrosion are not expected to occur, Hua et al. (2004).

3.5 Power Plant

Even gas fired power plants use titanium. One particular crystallizer system was designed with Gr12 tubes and Alloy 625 plate. Within months, Alloy 625 had failed by localized pitting corrosion. A quick repair with Alloy 276 failed in three days. The cause was failure to accurately identify the chemicals in the system. Higher levels of chloride, magnesium and iron where found in the cooling tower blowdown. The Gr12 tubes were not affected. However the Gr12 was later replaced to make the system more robust with Gr16, Gr7 and Gr26 materials, Heins and Solomon (2005).

3.6 Additional Geothermal

Geothermal systems are not immune to the occasional redesign. Great Lakes Chemical Company's geothermal bromine recovery plant near El Dorado, Arkansas USA is such an example. Total dissolved solids are near 286,000 ppm at 220°C with a pH range of 0 to 5. Lime or caustic and ammonia are used to raise the pH to a target of 5.5. The failure of one part led them to look at all of the materials in the process. Their selection criteria for a suitable titanium alloy for the rotor was based on reducing the susceptibility to stress corrosion cracking caused by chloride ions concentrating in pre-existing cracks. Titanium alloys containing aluminum, tin, manganese, cobalt and or oxygen greater than 0.317 percent are susceptible to this effect, Ellis (1980).

Tubular goods and rotors are not the only application for titanium in the geothermal industry. High strength, corrosion resistant metals are required for parts such as springs, snap-rings and the like. Most corrosion in geothermal environments and other similar applications described previously is caused by seven key corrosive species, Ellis et al. (1983).

- Oxygen (a good thing for reactive metals like titanium)
- Hydrogen Ion

- Carbon Dioxide
- Hydrogen Sulfide
- Ammonia
- Chloride Ion
- Sulfate Ion

Downhole conditions for geothermal applications can range from moderate to most severe. For this study we go to the most extreme case because most moderate conditions have already been studied and solved with grade 2, 7 or 12 titanium. The Salton Sea wells in southern California represent probably the most severe downhole environment encountered anywhere in the world. The synthetic brines used in this study will try and imitate the same conditions.

4. TEST PROCEDURE

The materials tested, Table 2, were all processed to flat sheet. All the samples received typical fabrication processing and included hot rolled, cold rolled, annealed, blasted, pickled, and machined to final width and length.

4.1 Mechanical Test

Tensile tests were completed per ASTM E8 standard with 1/8” x ¾” x 8” samples at room temperature at a rate of 0.005 in/in/min.

Hardness, unless noted was completed with a 10 kg load.

4.2 U-Bend Test

The U-bend test was determined with 1/8” x 0.60” x 5.12” samples according to ASTM G30 standards. An automated welder was optimized for each material to fully penetrate the sample autogenously down the center. The radius tested was 10T (1.25”) and the weld face became the OD after forming. The samples were not annealed and the root side of each was machined flat to remove any drop through.

4.3 Corrosion Test

A total of eleven titanium alloys and Alloy 625 were tested in the brine solution described below.

Total composition	Wt%	Qty
Water (H_2O)	79	1000 mL
Sodium Chloride (NaCl)	11.5	146 g
Calcium Chloride ($CaCl_2$)	6.3	80 g
Potassium Chloride (KCl)	2.4	30 g
Sodium Sulfide ($Na_2S(H_2O)_9$)	0.6	7.8 g
Hydrochloric Acid (HCl)	0.2	2.1 mL
Total dissolved solid count:		~205,000 ppm

Condition 1: ~104°C, Four days with solution changed every 24 hour. Each sample stood up in its own solution.

Condition 2: ~260°C, 7 days, solution was purged with nitrogen and a nitrogen blanket was added to the vessel prior to capping.

4.4 Crevice Corrosion

The crevice corrosion (CC) test entailed bolting PTFE washers to 1” x 1” material with an insulated ¼” bolt. The test materials all received a 3/8” wide weld autogenously down the center of the coupon and machined flat. The 5/16” hole was centered on the coupon. The welded coupon with PTFE washers were bolted together with 10in-lbs of torque. The solution was the same as that used for the corrosion test at a temperature of ~104°C for a period of 500 hours.

5. RESULTS AND DISCUSSION

Table 3 shows the results of the tensile, hardness and corrosion rate tests under condition 2 solution. The ultimate, yield values and elongation exceed ASTM requirements. The three experimental alloys, Ti 12+, 23+ and 38+ were higher than their similar alloys, Ti Grade 12, 23 and 38. Additional production runs and studies will need to be run to confirm this strength increase.

The hardness results ranged from 150-350 Vickers and are all consistent with standard production material. All the materials were examined metallographically to ensure an air contamination layer or other anomalies were not present in the material.

Corrosion results with condition 1 were good. All the alloys exhibited corrosion rate less than 0.5 mpy. They were all forwarded to the next testing condition.

Table 2. Chemistry of Materials Tested

Grade	Al%	V%	O%	N%	C%	Fe%	Ni%	Mo%	Other%
5	6.4	4.12	0.15	0.025	0.034	0.23			
7			0.11	0.002	0.01	0.09			0.16Pd
9	2.92	2.74	0.07	0.003	0.007	0.21			
12			0.13	0.004	0.01	0.11	0.81	0.31	
12+			0.21	0.01	0.02	0.11	0.8	0.3	Experimental Composition
23	6.01	3.95	0.09	0.006	0.02	0.19			
23+	6	3.95	0.1	0.016	0.023	0.18	T		Experimental Composition
28	2.87	2.5	0.09	0.006	0.008	0.14			.11Ru
36			0.07	0.006	0.007	0.02			45.1Nb
38+	4.1	2.6	0.26	T	0.02	1.4	T		Experimental Composition
6246	6.16		0.11	T			T	6.1	2Sn,4Zr
Alloy 625	0.22				0.04	4.45	59.9	8.32	22.7Cr, 3.4Nb, 0.24Si, 0.17Ti

Under condition 2 corrosion test grades 5 and 23 were expected to suffer general corrosion. Pitting of grade 12 was also predicted. Instead weight gain (WG) occurred on many of the Ti alloys, and by means of weight gain, an oxide film grew. The composition and thickness of the protective oxides that form on titanium alloys depend on environmental conditions. The oxide layer is typically less than 10 nm (100 Angstrom) thick.

Ti grade 9 was the only titanium alloy to show corrosion. The other Ti alloys did well with their alloying elements, Mo, Zr, Ni, Ru, and Pd. The nickel based alloy 625 showed signs of pitting and had a corrosion a rate of 0.46 mpy. None of the titanium alloy exhibited any pitting.

Table 3. Mechanical and Corrosion Test Results of the Twelve Alloys Tested in Condition 2 Solution.

Grade	Ultimate ksi	Yield ksi	% Elong.	Hardness Vickers	Corrosion mpy
Ti 5	160	153.6	14	351	WG
Ti 7	69	53.5	41	154	0
Ti 9	110	90	17	105 RB	0.55
Ti 12	75	58.8	33	183	WG
Ti 12+	111	91.1	21	235	0
Ti 23	139	134.4	16	312	WG
Ti 23+	153	147.7	12	340	WG
Ti 28	91	79.1	25	101 RB	WG
Ti 36	78	72.4	19	153	WG
Ti 38+	160	152.8	17	355	WG
Ti 6246	174	165.7	11	345	WG
Alloy 625	131	68	48	94 RB	0.46

Figure 1 shows the samples after condition 2 testing. The superficial discoloration is normal; a result of acidification and hydrolysis/passivation phenomena. In order of corrosion (top) to oxide protective (bottom eight) the alloys are grade 9, alloy 625, grade 7, 12+, 38+, 12, 23+, 28, 6246, 36, 5 and 23.

U-bend testing was conducted on all the alloys. A few of the alloys were tested at room temperature and performed without cracking including the three high strength experimental alloys 12+, 23+ and 38+. Ti grade 5 did not pass room temperature bending but did succeed with a warm forming temperature of 250°C. Many attempts to form Ti 6246 were conducted. Annealing the material and forming at room temperature did not work even though non-welded material was successful, see figure 2. Attempts at hot forming welded Ti 6246 up to 650°C also failed.

Although a majority of the welded alloys could be formed at room temperature, there was significant springback and what occurs in the lab may not occur in production. Annealing the material or warm forming is recommended.

Shown in figure 3 is an example of grade 23 that was welded and successfully U-bent. Each of the alloy materials had differing amounts of springback. This sample shown placed on its side would reveal a 90 degree angle.

Figure 1: Coupon Samples Showing Their Colors After Condition 2 Testing.

Figure 2: Ti 6246 Forming Results, Base and Welded Material.

Figure 3: Example of Welded Material After Forming, Gr23.

Crevice corrosion testing was conducted on a few of the alloys; 12+, 38+, Ti 6246 and Alloy 625. Of those samples tested only Alloy 625 exhibited crevice corrosion, see figure 4.

Figure 4: Crevice Corrosion of Alloy 625.

6. CONCLUSION

The results indicate excellent corrosion resistance for ten titanium alloys. Ti grade 9 and Alloy 625 also showed fairly good corrosion resistance near 0.5 mpy in the deaerated hot brine solution under pressure. Eight of the alloys tested displayed a thickened oxide layer (WG) which would benefit self healing in slurry type process streams.

Of all the materials tested the ones that did well in solution, passed welded U-bend forming at room temperature, and achieved an ultimate strength greater than 100ksi are: Ti grade 23 and experimental alloys 23+, 38+. This provides us with a basis for several improved titanium alloys to receive additional research. One could question the likelihood of Ti grade 23 passing stress corrosion cracking tests because it is similar to Ti grade 5 which is susceptible to that failure mode in hot chloride environments.

The solution chosen is a near likeness to hot process streams, geothermal brine wells, and deep sour gas well service. The only exception is the absence of H_2S and CO_2 gases. Additional testing of the ten titanium alloys that passed the corrosion test should be conducted with these gases added to the test solution. Another additional test would be to raise the temperature to 330°C, which would make conditions similar to the most extreme down-hole conditions being experienced in the geothermal industry today.

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